as follows: 1.10 kcal/mol for TBC, 1.93 kcal/mol for TBCC, and 3.46 kcal/mol for BCC. While the results for the TBC and TBCC forms are still reversed when compared with the energy minimization calculations, we nevertheless feel the agreement is sufficiently good to at least justify our use of these calculated strain energies as a guide in selecting which conformations to consider in the analysis.

Acknowledgments. The authors are deeply indebted to Professor Russell A. Bonham for the use of his electron diffraction facilities. We also wish to acknowledge the financial support of National Science Foundation Grants No. GP25673 and No. GP7423.

Supplementary Material Available. A tabulation of the raw intensity data and cartesian coordinates of the models will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8598.

Heats of Hydrogenation. X. Conjugative Interaction in Cyclic Dienes and Trienes

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Abstract: The heats of hydrogenation of the two cyclohexadienes, two cycloheptadienes, and three cyclooctadienes are reported and discussed in terms of empirical strain and conjugative interaction. The heats of hydrogenation of *cis*- and *trans*-hexa-1,3,5-triene are reported and related to those of cycloheptatriene, the two cyclooctatrienes, and cyclooctatetraene. Data on unsaturated cyclononanes and cyclodecanes can be interpreted to reveal the possible importance of adverse transannular interaction of suitably disposed pairs of double bonds. This hypothetical interaction is coupled with the Dewar–Schmeising theory of conjugative interaction to reinterpret the thermochemistry of several of the unsaturated cyclooctanes.

Heats of hydrogenation in acetic acid solution at 25° of various cyclic dienes and trienes as well as of the triene model compounds, *cis*-hexatriene, *trans*-hexatriene, and 1,5-hexadiene, are listed in Table I along with some related, but previously published data.[2,3] In view of the special properties associated with compounds possessing medium-sized rings, interpretation of much of the data is neither simple nor lacking in elements of uncertainty. We wish, however, to call attention to several items of interest that emerge from this work.

A reference point for a portion of the ensuing discussion is provided by *cis*- and *trans*-hexatriene, which are presumed to be strain-free and have the essentially planar conformations shown in the diagram, although the *cis*-triene possesses a slight twist (about 10°) at the central double bond.[4] If the validity of the theoretical treatment of Dewar and Haselbach[5] is accepted, such

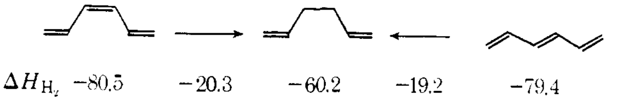

Table I. Heats of Hydrogenation in Acetic Acid Solution at 25°

Compound	$-\Delta H$, kcal/mol
Hexa-1,5-diene	60.17 ± 0.37
cis-Hexa-1,3,5-triene	80.50 ± 0.33
trans-Hexa-1,3,5-triene	79.43 ± 0.22
Cycloheptene	25.85 ± 0.09[a]
Cyclohepta-1,3-diene	49.92 ± 0.08
Cyclohepta-1,4-diene	55.88 ± 0.08
Cyclohepta-1,3,5-triene	70.49 ± 0.39[a]
cis-Cyclooctene	22.98 ± 0.10[b]
trans-Cyclooctene	32.24 ± 0.21[b]
Cycloocta-1,3-diene	48.96 ± 0.08
Cycloocta-1,4-diene	52.09 ± 0.28
Cycloocta-1,5-diene	53.68 ± 0.02
Cycloocta-1,3,5-triene	76.39 ± 0.44[c]
Cycloocta-1,3,6-triene	79.91 ± 0.17
Cycloctatetraene	97.96 ± 0.05[d]
cis-Cyclononene	23.62 ± 0.07[b]
trans-Cyclononene	26.49 ± 0.14[b]
cis,cis-Cyclonona-1,5-diene	46.32 ± 0.26
cis,trans-Cyclonona-1,5-diene	50.63 ± 0.32
cis,cis,cis-Cyclonona-1,4,7-triene	76.88 ± 0.05[e]
cis-Cyclodecene	20.67 ± 0.08[b]
trans-Cyclodecene	24.01 ± 0.09[b]
cis,cis-Cyclodeca-1,6-diene	43.73[f]
trans,trans-Cyclodeca-1,6-diene	47.63[f]
Cyclohexa-1,3-diene	53.64 ± 0.29
Cyclohexa-1,4-diene	53.90 ± 0.33

[a] Reference 2a. [b] Reference 2b. [c] A value of −72.36 ± 0.26 kcal/mol was previously published (ref 3) for this substance. The figure reported here is the average of six new determinations carried out at three different times over a period of 5 years. Explanation for the earlier low value has not been ascertained. [d] Reference 3. [e] W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yu, *J. Amer. Chem. Soc.*, **86**, 3178 (1964). [f] Sample sufficient for one run only.

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(2) (a) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957); (b) R. B. Turner and W. R. Meador, *ibid.*, **79**, 4133 (1957).

(3) R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *ibid.*, **79**, 4127 (1957).

(4) M. Traetteberg, *Acta Chem. Scand.*, **22**, 638, 2294 (1968).

(5) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

a minor deviation from planarity should obtain at negligible cost to π-electron delocalization. In both *cis*- and *trans*-hexatriene the central double bond is longer than the terminal double bonds (1.368 Å *vs.* 1.336 Å).

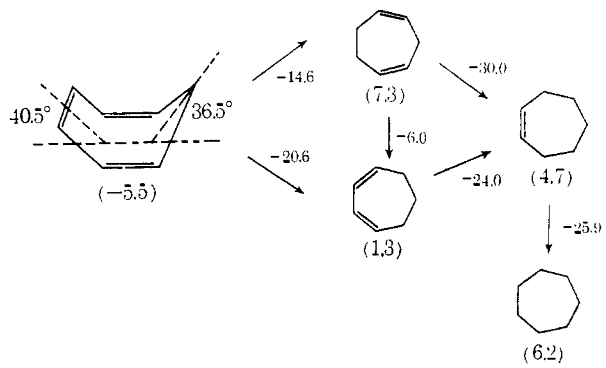
The hydrogenation data reveal a heat of isomerization of *cis*- to *trans*-hexatriene of -1.1 kcal/mol, which is identical for practical purposes with that of the isomerization of *cis*-butene to *trans*-butene (-1.0 kcal/mol).[6] Comparison of the heat of hydrogenation of the central double bond in *cis*-hexatriene (-20.3 kcal/mol) with those of *cis*-oct-4-ene (-27.4 kcal/mol)[7] and *cis*-1-isopropyl-2-methylethylene (-27.3 kcal/mol)[8] shows a lowering in the triene of about 7.1 kcal/mol. A similar result is derived from comparison of the heat of hydrogenation of the central double bond of *trans*-hexatriene (-19.2 kcal/mol) with that of *trans*-1-isopropyl-2-methylethylene (-26.4 kcal/mol).[8] It follows that conjugative interaction in planar or near planar trienes is twice that found in butadiene (3.6 kcal/mol)[9] in accord with the hypothesis of additivity advanced by Dewar and Schmeising.[10] It may be noted coincidentally that the heat of hydrogenation of *trans*-stilbene to 1,2-diphenylethane is almost identical (20.1 kcal/mol) with that of the central double bond in *trans*-hexa-1,3,5-triene.[11]

From the heats of formation of *cis*- and *trans*-hexatrienes, $\Delta H_f^\circ = +40.6$ and $+39.5$ kcal/mol, respectively (based on $\Delta H_f^\circ = -39.92$ kcal/mol for *n*-hexane),[12] an alternative model for the resonance energy of benzene can be constructed which more nearly reveals the magnitude of the purely cyclic component. The difference in heats of formation between two molecules of ethylene and one of butadiene ($+1.21$ kcal/mol) and between one molecule each of ethylene and butadiene and one of *trans*-hexatriene ($+0.94$ kcal/mol) may be taken to represent the expected ($+1.08$ kcal/mol) heat of dehydrogenation of *trans*-hexatriene (trans is taken rather than cis because of the disappearance in the cyclization of those factors responsible for the incremental heat of formation in the cis isomer) to benzene and hydrogen. Comparison with the heat of the reaction based on actual heats of formation reveals a discrepancy of $+20.8$ kcal/mol as the "resonance energy" of benzene.

Other trienes available for assessment of consistency of their stabilization pattern are cyclic and hence cisoid. They are cyclohepta-1,3,5-triene and cycloocta-1,3,5-triene. In view of the severity of nonbonded interactions in rings of medium size, the conjugative interaction of double bonds in these systems seems best analyzed in terms of minimum strain energies which can be estimated from heats of hydrogenation and from the strain energies of cycloheptane and cyclooctane in the following manner.

The vapor phase heat of formation of cycloheptane is -28.21 kcal/mol.[13] If the heat of formation of a hypothetical strain-free cycloheptane is taken to be 7/6 that of cyclohexane, *i.e.*, -34.41 kcal/mol, the strain energy of cycloheptane becomes $+6.20$ kcal/mol.[14] The heat of hydrogenation of cycloheptene to cycloheptane (acetic acid solution, 25°) is -25.9 kcal/mol or 1.5 kcal/mol less than the value for *cis*-oct-4-ene of -27.4 kcal/mol[7] (taken throughout this analysis as the reference heat of hydrogenation of a typical cis olefin to an unstrained paraffin hydrocarbon). This discrepancy of 1.5 kcal/mol is equated with the difference in strain between cycloheptane and cycloheptene, which is thus assigned an empirical strain energy of 4.7 kcal/mol. Other values similarly derived for additional members of the series are given in parentheses in Scheme I. These values would all be changed by the same amount if a base value other than 6.2 kcal/mol for cycloheptane were selected.[14] To the extent that conjugative interaction between the double bonds lowers the heat content of cyclohepta-1,3-diene and cyclohepta-1,3,5-triene, the energy associated with strain is greater (more positive) than that indicated.

Scheme I



It is of particular interest that cyclohepta-1,3,5-triene emerges with a physically meaningless negative "strain." Such an occurrence must point to a conjugative interaction 5.5 kcal/mol greater than the total strain within the molecule. It appears to us that no closer specification of the conjugative interaction can be made. In retrospect it appears that the method of estimation employed earlier[15] gave such similar results (6.7 kcal/mol) only through the fortuity that the difference between the strain energy in cycloheptane and cycloheptene is small. If the conjugative interaction is set equal to that in *trans*-hexa-1,3,5-triene (7.1 kcal/mol) or to twice that in butadiene (7.2 kcal/mol), a strain energy of 1.6 kcal/mol is indicated in cyclohepta-1,3,5-triene. The geometry of cyclohepta-1,3,5-triene can be inferred from the X-ray analysis by Davis and Tulinsky[16] of thujic acid, but has been determined directly in the gas phase by electron diffraction by Traetteberg.[17] The central double bond lies in a plane at a dihedral

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(6) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **58**, 137 (1936).

(7) R. B. Turner, A. D. Jarrett, P. Goebel, and B. J. Mallon, *ibid.*, **95**, 790 (1973).

(8) R. B. Turner, D. E. Nettleton, and M. Perelman, *ibid.*, **80**, 1430 (1958).

(9) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, **58**, 146 (1936).

(10) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960).

(11) R. B. Williams, *J. Amer. Chem. Soc.*, **64**, 1395 (1942).

(12) A critical, convenient collection of heats of formation is available: J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

(13) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, *J. Amer. Chem. Soc.*, **78**, 5469 (1956).

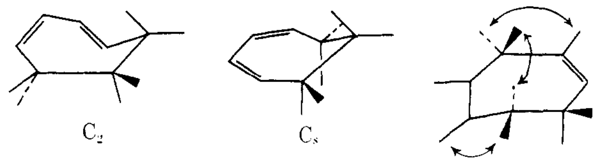
(14) The single conformation increment of P. v. R. Schleyer, J. E. Williams, and K. R. Banchard [*ibid.*, **92**, 2377 (1970)] gives a somewhat higher value (7.57 kcal/mol).

(15) J. Conn, G. B. Kistiakowsky, and E. Smith, *J. Amer. Chem. Soc.*, **61**, 1868 (1939).

(16) R. E. Davis and A. Tulinsky, *Tetrahedron Lett.*, 839 (1962).

(17) M. Traetteberg, *J. Amer. Chem. Soc.*, **86**, 4265 (1964).

angle of 40.5° (23.7°)[16] to the plane occupied by the other two double bonds while the methylene group lies at a dihedral angle of 36.5° (49.7°).[16] It is noteworthy that the apparent conjugative interaction is so little affected by the change from trans planar in *trans*-hexa-1,3,5-triene to cis nonplanar in cycloheptatriene.



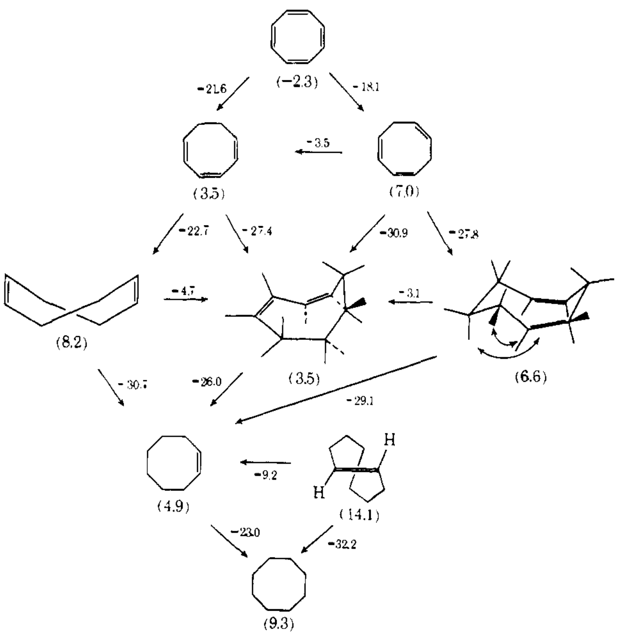
Of two conformations of cyclohepta-1,3-diene, C_2 has a dihedral angle of about 45° between the planes occupied by the double bonds, two severe H–H repulsions, two adverse interactions at 2.52 Å between each double bond and an opposite H, and the methylene hydrogens not quite staggered but far from eclipsed.[18] Conformation C_s, achieved by expansion of the internal diene angles to 129°, has imperfect staggering of methylene hydrogens, only one severe H–H repulsion, and all carbon atoms except the methylene at C_6 lying in the same plane. This "planar" C_s conformation is indicated by the electron diffraction investigation of Chiang and Bauer[19] and fully confirmed by Hagen and Traetteberg.[18] The change in ultraviolet absorption of cyclohepta-1,3-diene (248 nm)[20] *vis-à-vis* that of cyclohexa-1,3-diene (256 nm)[21] is more easily reconciled with structure C_2 than with C_s,[22] but nothing based either upon analogy or theory can be predicted about the effect of expansion of the bond angles in C_s on the position of ultraviolet absorption. More difficult to reconcile with the planar-but-for C_6 structure (C_s) is the nmr coupling constant between H(C_2) and H(C_3) in which Crews[23a] finds strong indication of the C_2 structure. The logic of this conclusion involves an empirical correlation of coupling constants with angles of twist indicated in diffraction studies of a number of conjugated di- and trienes.[23b] Until this contradiction is resolved by reference to one or more independent criteria of structure, it may serve as well to weaken the nmr component of the correlation as the electron diffraction component.[24]

The preferred conformation of cyclohepta-1,4-diene is not known, but in that chiral conformation assumed in a Dreiding model (and in the conformation halfway between the enantiomers), there are several severe nonbonded repulsions which could account for as much as 7.3 kcal/mol of strain.

Of considerable interest is the difference of 6.0 kcal/mol in the empirical strain estimated for cyclohepta-1,3-diene and cyclohepta-1,4-diene. Since inspection of models suggests considerable crowding in both dienes, the apparent lowering of strain in the 1,3 diene may reasonably be associated with a conjugative stabilization.

Analysis of the eight-membered ring series is based upon a strain energy in cyclooctane of 9.3 kcal/mol.[25] Granted that the standard heat of hydrogenation of a cis double bond be −27.4 kcal/mol,[7] the empirical strain energies of the unsaturated members of the series assume the following values (Scheme II): *cis*-cyclooctene, 4.9; *trans*-cyclooctene, 14.1; cycloocta-1,5-diene, 8.2; cycloocta-1,3-diene, 3.5; cycloocta-1,4-diene, 6.6; cycloocta-1,3,5-triene, 3.5; cycloocta-1,3,6-triene, 7.0; and cyclooctatetraene, −2.3 kcal/mol. A small negative empirical strain thus appears in cyclooctatetraene. Although cycloocta-1,3,5-triene, unlike cyclohepta-1,3,5-triene, does not show a negative strain, its strain energy is lower (3.5 kcal/mol) than that of cycloocta-1,3,6-triene, by an amount essentially identical with the conjugative interaction of butadiene, 3.6 kcal/mol.[9] A further discussion of this point is given below.

Scheme II



Although the conformation of cycloocta-1,4-diene has not been determined, the best recognizable from models and shown in Scheme II retains nonbonded interactions compatible with the considerable strain (6.6 kcal/mol). Cycloocta-1,5-diene has been shown to be a polar molecule and hence probably to possess the flexible tub conformation.[26] Anet and Kozerski,[27] in a recent, elegant investigation of the ^{13}C and ^1H nmr spectra at very low temperatures, find convincing evidence for the twisted boat (or tub) structure shown in Scheme II. The crowding in the structure is consistent with the low activation energies of interconversion[27] as well as with the considerable empirical strain of 8.2 kcal/mol. This conformation is favored in recent calculations of Allinger and Sprague[28] in which a heat

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[18] K. Hagen and M. Traetteberg, *Acta Chem. Scand.*, **26**, 3643 (1972).

[19] J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **88**, 420 (1966).

[20] E. Pesch and S. L. Friess, *ibid.*, 72, 5756 (1950).

[21] H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).

[22] *Cf.* E. A. Braude, *Chem. Ind.* (*London*), 1557 (1954).

[23] (a) P. Crews, *Chem. Commun.*, 583 (1971); (b) D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *J. Amer. Chem. Soc.*, **91**, 5286 (1969).

[24] In a recently completed calculation, N. L. Allinger and J. T. Sprague, *Tetrahedron*, **29**, in press, have discovered that very little difference in energy is to be expected between C_s and C_2 and that the molecule may be an equilibrium mixture.

[25] The difference between the heat of formation of cyclooctane (+30.06 kcal/mol[13]) and 8/6 that of cyclohexane. If the Schleyer value[14] of 11.0 kcal/mol seems preferable, empirical strain energies in the ensuing discussion may be increased by 1.7 kcal/mol.

[26] W. Klemperer, *J. Amer. Chem. Soc.*, **92**, 6325 (1970).

[27] F. A. L. Anet and L. Kozerski, *ibid.*, **95**, 3407 (1973).

[28] N. L. Allinger and J. T. Sprague, *ibid.*, **94**, 5734 (1972).

Table II. Molecular Parameters of Conjugated Cycloalka-1,3-dienes

Parameter	C_6H_8[a]	C_7H_{10}[b]	C_8H_{12}[c]
$C_1{=}C_2$ (Å)	1.348	1.347	1.347
$C_2{-}C_3$ (Å)	1.465	1.450	1.475
$C_4{-}C_5$ (Å)	1.519	1.509	1.509
$C_5{-}C_6$ (Å)	1.538	1.522	1.542
$\angle C_1C_2C_3$ (deg)	120.3	129.1	129.0
Dihedral $\angle$ (deg)	18.0	0.0	37.8

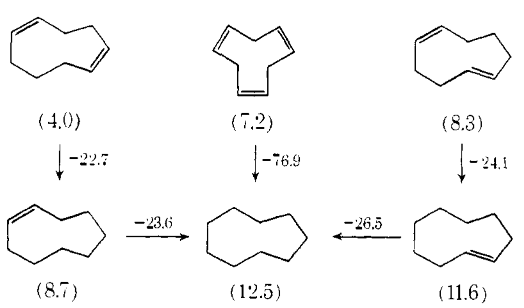
[a] M. Traetteberg, *Acta Chem. Scand.*, **22**, 2305 (1968). [b] Reference 18. [c] Reference 29.

of hydrogenation of 31.8 kcal/mol is predicted for the first double bond. The agreement with the experimental value of 30.7 kcal/mol is excellent.

Cycloocta-1,3-diene, the conformation of which has been established by Traetteberg[29] by application of the electron diffraction method, has a substantially smaller empirical strain energy than that calculated for its two unconjugated isomers. The conformation is largely determined by a dihedral angle 37.8° between the planes occupied by the double bonds. It may be approximated with Dreiding models by twisting the C_2, tub-like conformation part way toward the conformation with the double bonds coplanar (until $C_5 \cdots C_8$ becomes 3.02 Å or 7.56 cm in the model).

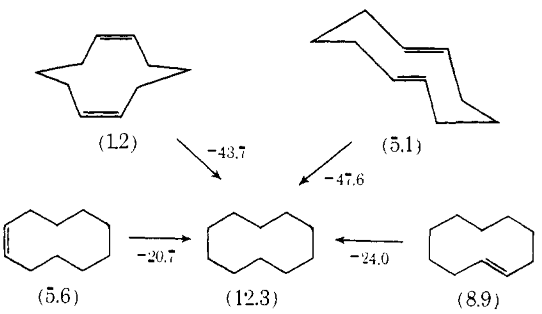
The ultraviolet absorption of this diene (228 nm)[22] is in agreement with a nonplanar conformation. If butadiene-type stabilization (3.6 kcal/mol) be admitted, the total strain in cycloocta-1,3-diene becomes 7.1 kcal/mol. This value is in better accord (than the value of 3.5 kcal/mol) with the severe strain inferred from expansion of the two internal angles of the diene, the closeness of approach of H_7 to the C_3–C_4 double bond, the proximity of H_{5a} and H_{8a}, and the eclipsing of hydrogens at C_7 and C_8.

Of special interest is the persistance of a high level of strain in most of the unsaturated eight-membered ring compounds despite the expectation that replacement of adjacent methylene groups by *olefinic* linkages should lower strain by reducing the number of transannular hydrogen–hydrogen repulsions. In fact, only with the introduction of the first double bond in *cis*-cyclooctene is strain reduction, uncomplicated by conjugative interaction, observed.



This phenomenon is also encountered in the few members of the nine-membered ring series that have been available for investigation. Thus the 12.5 kcal/mol of strain in cyclononane[30] is reduced in both *cis*- and *trans*-cyclononene and in the 1,5 dienes as well, but the strain in *cis,cis,cis*-cyclonona-1,4,7-triene is greater by 3.2 kcal/mol than that in *cis,cis*-cyclonona-1,5-diene. *cis,cis,cis*-Cyclonona-1,4,7-triene has been determined by X-ray analysis to have the crown structure.[32] The approach of the three intraannular hydrogen atoms, 1.95 Å, is closer than the van der Waal's distance of 2.2 Å and has been noted as the probable origin of some of the strain in this molecule. We suggest that another part may be associated with the cis-parallel 1,4-pentadiene system.

Adverse interaction between transannular double bonds can also be inferred in the cyclodecane series. The empirical strain energies obtained in the usual manner are given in the diagram. The introduction of the first double bond (regardless whether cis or trans)



leads to a reduction in strain. There is a further reduction in proceeding to *cis,cis*-cyclodeca-1,6-diene for which an apparently strain-free structure has been established by the electron diffraction method.[33] In this structure the two double bonds are widely separated and, owing to their cis nature, should impart a residual strain of *ca.* 2.0 kcal/mol. The present results seem excellent confirmation of the strain-free nature. Although we had no other isomers available at the time, this investigation should be the more interesting in the light of the experience of Hubert and Dale[34] who find *only* the cis,cis-1,6 isomer after the apparent establishment of equilibrium by base catalysis with sodium–alumina at 25°. A strain-free model can be made for the trans,trans isomer by cutting cyclohexane in the chair conformation in half and inserting two parallel trans double bonds.[35] Since the structure of this isomer has not been established, it can be no more than a suggestion that its strain originates in the enforced interpenetration of the van der Waals profiles of the two double bonds. Roth has provided qualitative confirmation of the enthalpy difference between trans,trans and cis,cis in a kinetic investigation at 230–250° in which equilibrium is found to lie entirely on the side of the cis,cis isomer.[36] In the model of Grob and Schiess, the estimated distance of approach (2.67 Å) is considerably less than the estimated value, 3.20 Å, for the closest unstrained par-

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[29] M. Traetteberg, *Acta Chem. Scand.*, **24**, 2285 (1970).

[30] The discrepancy between the heat of formation of −31.73 kcal/mol reported by S. Kaarsemaker and J. Coops [*Recl. Trav. Chim. Pays-Bas*, 71, 261 (1952)] and the strain-free value calculated as 9/6 of the heat of formation of cyclohexane. Use of Schleyer's single conformation increment gives a strain energy of 14.4 kcal/mol.[14]

[31] Base-catalyzed (KO-*t*-Bu–DMSO at 70°) equilibration shows 6% of cyclonona-1,3-diene, a trace of the 1,4-diene, and 94% of cyclonona-1,5-diene, from which it is safely assumed that the strain in the first two is even greater: D. Devaprahakara, C. G. Cardenas, and P. D. Gardner, *J. Amer. Chem. Soc.*, **85**, 1553 (1963).

[32] W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yü, *J. Amer. Chem. Soc.*, **86**, 3178 (1964).

[33] A. Almenningen, G. G. Jacobsen, and H. M. Siep, *Acta Chem. Scand.*, **23**, 1495 (1969).

[34] A. J. Hubert and J. Dale, *J. Chem. Soc. C*, 188 (1968).

[35] (a) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **47**, 558 (1964); (b) D. N. J. White, *ibid.*, **56**, 1347 (1973).

[36] W. R. Roth, *Chimia*, 20, 229 (1966).

allel approach of two benzene rings.[37] It should be noted that the recent calculations by Allinger and Sprague[28] fail to bring out the difference [calcd ΔH_{H_2} = 21.36 and 22.72 *vs.* exptl 20.67 and 24.01 kcal/mol, respectively] between *cis*- and *trans*-cyclodecene and indicate 6 kcal/mol of strain in *cis,cis*-cyclodeca-1,6-diene (but based on a different strain-free model from that used here or by Schleyer, Williams, and Banchard[14]).

It may be suggestive that the orientation of the two double bonds in the recently determined structure of 2,7-dibromo-3,8-dimethoxycyclodeca-*trans*-1,*trans*-6-diene is *not* opposed as in the Grob structure.[35b]

The hypothetical association of a significant amount of strain with adverse transannular interaction between two double bonds brings the otherwise anomalous molecules, cycloocta-1,3,5-triene and cyclooctatetraene, into consistency with cyclohepta-1,3,5-triene. If, for the sake of discussion alone, the value of this repulsion at the distance and orientation of the eight-membered rings is assumed to be 6 kcal/mol, the total strain in cyclooctatetraene becomes 12 kcal/mol and the total conjugative interaction becomes 14.3 kcal/mol or essentially identical with 4 × 3.6 kcal/mol and no longer has the implausibly low value of 2.3 kcal/mol. Similarly, the total strain in cycloocta-1,3,5-triene becomes 9.3 kcal/mol and is nearly balanced by two elements of conjugative interaction.

In these terms, the remarkably high strain of cycloocta-1,5-diene would be ascribed to transannular repulsion in the tub conformation and that of cycloocta-1,6-diene to its *cis*-1,4-pentadiene unit. The otherwise perplexingly high strain in cycloocta-1,3,6-triene could be similarly rationalized.

We wish to emphasize that the two elements in this discussion, transannular van der Waals repulsion between double bonds and the sp^2–sp^2 σ-bond conjugative interaction of Dewar and Schmeising, both stand in further need of quantitative assessment and may not be construed to have acquired credibility from having introduced a semblance of order into this collection of data. This discussion will have served its purpose if Allinger's recent assessment of the state of affairs: "Thus olefins and cyclopropanes are not in principle amenable to treatment by the present scheme (as it now stands)," [38] is replaced by proper van der Waals functions for the double bond.[26,39]

In 1936 Kistiakowsky and his associates[9] reported a value of −55.4 kcal/mol for the heat of hydrogenation of cyclohexa-1,3-diene in the vapor phase. Conventional comparison of this result with twice the cyclohexene figure (2 × 28.6 kcal/mol) led to the conclusion that cyclohexa-1,3-diene possessed 1.8 kcal/mol of conjugative stabilization. We have now provided solution values for both cyclohexa-1,3-diene (−53.6 kcal/mol) and cyclohexa-1,4-diene (−53.9 kcal/mol). It is evident that within the limits of experimental uncertainty the heat of isomerization is negligible. This conclusion is supported by the equilibrium data[40] which give a free energy difference between the conjugated and unconjugated isomer at 110° of −0.41 kcal/mol.

Since we can see little basis for assuming important steric differences between the 1,3 and 1,4 isomers, we conclude that cyclohexa-1,3-diene is devoid of conjugative stabilization and that interaction of the butadiene type is counterbalanced by other factors (possibly π-cloud repulsion) in this planar cisoid system.

The vanishing of conjugative interaction in cyclohexadienes is a general phenomenon,[40b] but seems not to be carried over to nonplanar cisoid dienes such as cycloocta-1,3-diene. Traetteberg has made important contributions to the question of relating conjugative interaction to dihedral angle, particularly in establishing that the sp^2–sp^2 σ-bond distance of 1.46 Å prevails in cycloocta-1,3-diene at the dihedral angle of 38°.[26] Equilibrium studies fully confirm the degree to which enthalpy favors the conjugated diene in the seven-[41] and eight-membered rings.[41,42] Only the planarity of cyclohepta-1,3-diene is in discord with the otherwise consistent hypothesis of Traetteberg[43] that the second minimum in dienes occurs at 30°, not 0°, and involves little difference in energy from the first, 180°, minimum.

Experimental Section

Materials. Cyclohexa-1,3-diene was prepared according to Grob and Hostynek,[44] purified by glpc on a silicone column (3 m × 0.5 in. 20% Dow Silicon Fluid 710 on 40–60 mesh kieselguhr), and characterized by uv, ir, nmr, and mass spectra. In the absence of hydroquinone, a freshly distilled sample open to the air at 4° had absorbed enough oxygen to color KI–CH_3COOH solution yellow.

Cyclohexa-1,4-diene, purchased from K and K Laboratories, bp 89°, was purified by glpc on the silicone column and identified spectroscopically. Although it also absorbed oxygen, the rate seemed much slower.

Cyclohepta-1,3-diene was prepared by analogy with the method used for cyclohexa-1,3-diene. (a) Suberone (250 g) in 300 ml of ether was added dropwise with cooling at −20° to a suspension of $LiAlH_4$ (50 g) in 1000 ml of ether over a 3-hr period, boiled under reflux for 1 hr, and worked up in the usual manner to give cycloheptanol (210 g), bp 92° (25 mm). (b) Distillation with 4 g of naphthalene-β-sulfonic acid afforded cycloheptene (150 g), bp 111–113°. (c) Following the addition of 2 g of dibenzoyl peroxide to boiling cycloheptene (150 g), *tert*-butyl hypochlorite (80 g)[45] was added dropwise at such a rate to maintain regular boiling. After boiling under reflux for 15 min, the mixture was distilled to afford 3-chlorocycloheptene (35 g), bp 69° (28 mm). (d) Slow distillation at 120° of a mixture of 3-chlorocycloheptene (35 g) and dimethylaniline (77 g) afforded cyclohepta-1,3-diene; after redistillation, 13 g, bp 121.5–123°, material contained *ca.* 10% impurities reduced to 1% by purification on the preparative silicone column (95°, N_2 gas, 0.5-ml injected sample), identified by ir, nmr, and uv, λ_{max} 247 nm (ϵ_{max} 8100).

Cyclohepta-1,4-diene, generously furnished by Professor E. Vogel, University of Cologne, was purified by glpc on a silicone column. Identification was confirmed by ir, uv, and nmr spectra.

The isomeric 1,3-, 1,4- and 1,5-cyclooctadienes were prepared by the reduction of cyclooctatetraene[46] according to the method of Craig, *et al.*,[47] and purified by recrystallization of the silver nitrate complexes according to the method of Jones.[48]

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[37] D. E. Williams, *J. Chem. Phys.*, **47**, 4680 (1967); R. H. Boyd, *Tetrahedron*, **22**, 119 (1966); C. Shieh, D. C. McNally, and R. H. Boyd, *ibid.*, **25**, 3653 (1969).

[38] N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968).

[39] N. L. Allinger and J. T. Sprague, *ibid.*, **95**, 3893 (1973).

[40] (a) W. von E. Doering, G. Schröder, K. Trautner, and S. Staley, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 14M; (b) S. Staley, Ph.D. Dissertation, Yale University, 1964; (c) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, **85**, 3032 (1963).

[41] W. von E. Doering and G. Schröder, unpublished; base-catalyzed equilibration leads completely to conjugated isomers.

[42] H. A. Tayim and A. Vassilian, *Chem. Commun.*, 630 (1970).

[43] M. Traetteberg, *Acta Chem. Scand.*, **24**, 2295 (1970).

[44] C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1973).

[45] H. M. Teeter and E. W. Bell, "Organic Syntheses," Collect. Vol. 4, Wiley, New York, N. Y., 1963, p 125.

[46] We express our gratitude to Badische Anilin und Sodafabrik, Ludwigshafen, for a generous sample of cyclooctatetraene.

[47] L. E. Craig, R. M. Elofson, and I. J. Ressa, *J. Amer. Chem. Soc.*, **75**, 480 (1953).

[48] W. O. Jones, *J. Chem. Soc.*, 312 (1954).

The crude mixture (30 ml), consisting mainly of 1,4- and 1,5-cyclooctadiene, was converted to a mixture of 1,3- and 1,5-cyclooctadiene by treatment for 12 hr at 140° with a solution of sodium (20 g) in *tert*-amyl alcohol (150 ml).

The dienes were recovered from the purified silver nitrate complexes by steam distillation and distillation at atmospheric pressure in purity greater than 99% by glpc on a silicone column. Each sample was identified by ir and nmr spectra: cycloocta-1,3-diene, bp 141.0°, λ_{max} 227 nm (ϵ_{max} 6160); cycloocta-1,4-diene, bp 143.0°; cycloocta-1,5-diene, bp 148.5°.

Cycloocta-1,3,5-triene was prepared according to Jones.[49] It was freed of bicyclo[4.2.0]octa-2,4-diene by treatment with maleic anhydride according to the procedure of Cope, *et al.*[50]

Cycloocta-1,3,6-triene was prepared by the procedure of Sanne and Schlichting.[51] The substance was separated from accompanying cycloocta-1,3,5-triene by distillation in a 1-m spinning band column. Any bicyclo[4.2.0]octa-2,4-diene was removed by shaking at 50° with maleic anhydride.

cis- and *trans*-Hexa-1,3,5-triene were prepared according to Hwa, DeBenneville, and Svens.[52]

Professor E. Vogel and Dr. E. Dinne kindly supplied samples of *cis,cis*- and *cis,trans*-cyclonona-1,5-diene.

Samples of *cis,cis*- and *trans,trans*-cyclodeca-1,6-dienes were prepared in the laboratory of Professor W. R. Roth, Cologne, according to the procedure of Heimbach.[53]

Calorimetric Measurements. Heats of hydrogenation were measured in the apparatus, and by the general procedure, described earlier.[2a] The solvent consisted in all runs of 225 ml of prereduced acetic acid. Samples of olefins sufficient to provide for an uptake of approximately 3 mmol of hydrogen were introduced in evacuated, sealed ampoules. Hydrogenation was initiated by breaking an ampoule containing approximately 100 ml of PtO_2 catalyst, which had been calibrated previously with respect to hydrogen absorption and heat evolution. Although calculations are based on the amount of hydrogen absorbed, there was essentially quantitative absorption of hydrogen in all cases.

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(49) W. O. Jones, *J. Chem. Soc.*, 1808 (1954).

(50) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4867 (1952).

(51) W. Sanne and O. Schlichting, *Angew. Chem.*, **75**, 156 (1963).

(52) J. C. H. Hwa, P. L. DeBenneville, and H. J. Svens, *J. Amer. Chem. Soc.*, **82**, 2537 (1960).

(53) P. Heimbach, *Angew. Chem.*, **78**, 604 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 595 (1966).

Calorimetric and Equilibrium Studies on Some Stable Nitroxide and Iminoxy Radicals. Approximate O–H Bond Dissociation Energies in Hydroxylamines and Oximes

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Abstract: The differences in the heats of formation in solution of the stable free radicals, 2,2,6,6-tetramethylpiperid-4-one 1-oxyl (**1a**), 2,2,6,6-tetramethylpiperdine *N*-oxyl (**1b**), and di-*tert*-butyliminoxy (**2**), and their hydrogenated precursors have been determined by a direct calorimetric technique. The equilibrium constants for the hydrogen atom transfer reactions of these radicals with certain hydroxylamines and oximes were then determined by the epr spectroscopic method. The analysis of the results of these experiments leads to the predictions that the O–H bond strengths of unhindered dialkylhydroxylamines are in the range of 72–74 kcal/mol while the O–H bond strengths of simple unhindered oximes are equal to approximately 86 kcal/mol.

Since bond dissociation energies of organic molecules are normally determined by experiments in the gas phase, the types of molecules for which reliable values are available cover only a small fraction of the molecules of interest to organic chemists. An important extension of bond dissociation energy data to larger and less volatile molecules was the first direct calorimetric determination of the differences in the heats of formation in solution of a radical, 2,4,6-tri-*tert*-butylphenoxy (A·), and its parent, 2,4,6-tri-*tert*-butylphenol (AH), reported by one of us in 1969.[3] This difference, *i.e.*, $(\Delta H_f)_{A\cdot}^{solvent} - (\Delta H_f)_{AH}^{solvent}$, yields the O–H bond strength in the phenol *provided* the difference in the heats of formation of the radical in the gas phase and in solution at infinite dilution is equal to the difference in the heats of formation of the phenol in the same two states, *i.e.*, provided that

$$(\Delta H_f)_{A\cdot}^{gas} - (\Delta H_f)_{A\cdot}^{solvent} = (\Delta H_f)_{AH}^{gas} - (\Delta H_f)_{AH}^{solvent}$$

In the absence of a *specific* interaction involving *either* the radical *or* the phenol and the solvent this equality is expected to be true to within ±2 kcal/mol and few bond dissociation energies of polyatomic molecules are known with much greater precision. There is not likely to be any specific solvent effect particular to the highly hindered A· or AH in the solvents employed (CCl_4, benzene, and chlorobenzene). We can therefore calculate an approximate bond dissociation energy for AH from the relation

$$D[A-H] \approx (\Delta H_f)_{A\cdot}^{solvent} - (\Delta H_f)_{AH}^{solvent} + (\Delta H_f)_{H\cdot}$$

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(3) L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, *J. Amer. Chem. Soc.*, **91**, 3883 (1969).